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(71) Applicant(s)

Nippon Paint Co., Ltd.
(Incorporated in Japan)
1-2, Oyodokita 2-chome, Kita-ku, Osaka-shi,
Osaka-fu, Japan

(72) Inventor(s)

Takao Morimoto
Takeshi Takagi
Hisaki Tanabe

(74) Agent and/or Address for Service

Reginald W Barker & Co
Chancery House, 53-64 Chancery Lane, LONDON,
WC2A 1QU, United Kingdom

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(54) Abstract Title

Hydrophilic resin and water-based paint

(57) For providing heat-curable water-based paints with high structural viscosity and improving their resistance to sagging and popping, a copolymer of a carboxyl-terminated (meth)acrylate ester monomer, a hydroxyl-containing ethylenically unsaturated monomer and an acrylic monomer containing a saturated hydrocarbon group containing 6 to 18 carbon atoms, optionally together with another ethylenically unsaturated monomer is grafted onto a hydroxyl-terminated polyester resin by transesterification, the acryl-grafted polyester resin is neutralized with a base and dispersed in an aqueous medium, together with a curing agent and a pigment.

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HYDROPHILIC RESIN AND WATER-BASED PAINT

FIELD OF THE INVENTION

The present invention relates to a hydrophilic resin,
5 a water-based paint comprising the same, a method of
coating which comprises applying said composition, and
a coated article.

BACKGROUND ART

10 From the concern about environmental pollution, the
interest in paints free of any organic solvent is mounting.
One proposed solution is the use of water-based paints.
One of the problems intrinsic in water-based paints is
that the workability and the appearance of finished
15 surfaces are readily influenced by humidity. Thus, in
a high humidity environment, sagging and popping tend to
appear, detracting from the finish appearance. This is
particularly serious in the field of automobiles, for
instance, where high regard is paid to the appearance.

20 Sagging and popping are related to the viscosity and
nonvolatile matter content of the paint at the time of
application. Thus, the higher the viscosity or
nonvolatile matter content is, the less liable is the
occurrence of sagging and popping. However, at the time
25 of coating, the viscosity must be decreased to a level
at which coating is possible but such a low viscosity can
hardly be reconciled with a high nonvolatile matter
content. One means for solving this problem comprises
using the vehicle resin in the form of a dispersion system,
30 such as an emulsion or a sol, to thereby provide for
structural viscosity. This leads to a decrease in
apparent viscosity coefficient upon application of a
shear stress at the time of coating, so that the
workability requirement can be satisfied. After
35 covering the article to be coated and removal of the shear

stress, the apparent viscosity coefficient increases, making sagging difficult to occur. Since no drastic decrease in nonvolatile matter content is required, the problem of popping can be solved as well. The increase of apparent viscosity of the coating film on the substrate is not dependent on the evaporation of water and therefore the occurrence of sagging and popping is not influenced by the humidity in the painting environment.

A number of water-based paints embodying the above idea have so far been proposed. These can be roughly classified into two categories: in one, a particle suspension comprising a different component is added, as typically disclosed in Japanese Kokai Tokkyo Koho H04-25582 and H08-12925 and, in the other, a resin suspension is used in which cores made of a hydrophobic resin are each coated with a shell made of a hydrophilic resin, as typically disclosed in Japanese Kokai Tokkyo Koho H04-233926 and H07-74320. However, these cannot simultaneously satisfy the requirements concerning the degree of expression of structural viscosity, storage stability of paints, and performance characteristics of cured coating films inclusive of water resistance.

The water-based paint of the present invention belongs to the latter category, namely the resin suspension type comprising the core of a hydrophobic resin and the shell of a hydrophilic resin and yet can satisfy all the requirements concerning the expression of structural viscosity, storage stability, and performance characteristics of cured coating films.

SUMMARY OF THE INVENTION

The present invention provides a hydrophilic resin which comprises 50 to 90% by weight of an acrylic resin (A) and 50 to 10 % by weight of a polyester resin (B), said acrylic resin (A) being graft-bonded to said

polyester resin (B) by means of transesterification, wherein said acrylic resin (A) comprises of a carboxyl-terminated acrylic monomer (a), a hydroxyl-containing acrylic monomer (b) and an acrylic monomer (c) containing a saturated hydrocarbon group containing 6 to 18 carbon atoms, and has an acid value of 10 to 100, a hydroxyl value of 50 to 300 and a number average molecular weight of 5,000 to 100,000.

The present invention also provides a water-based paint which comprises said hydrophilic resin and a curing agent, both dispersed in an aqueous medium containing a neutralizing base.

The present invention also provides a method of coating by two coat one bake technique which comprises applying the above water-based paint to a substrate and then applying a clear paint, followed by baking.

In a still further aspect, the present invention provides a coated article having a coat resulting from application of the water-based paint mentioned above.

20

DETAILED DESCRIPTION OF THE INVENTION

The above-mentioned carboxyl-terminated acrylic monomer (a) is such that the position of the carboxyl group is remote from the carbon atoms constituting the main chain, and said acrylic monomer (c) containing a saturated hydrocarbon group containing 6 to 18 carbon atoms contains a saturated hydrocarbon group which is bulky and hydrophobic. Therefore, when said hydrophilic resin is neutralized and dispersed in water, the carboxyl group remote from the main chain of monomer (a) serves to increase the thickness of the hydrated layer of the shell, while the bulky saturated hydrocarbon group of monomer (c) interacts with another such group in water in the manner of mutual repulsion. As a result, said hydrophilic resin acquires a high structural viscosity

and the thixotropy index (TI value) increases.

Said hydroxyl-containing acrylic monomer (b) has a hydroxyl group capable of reacting with the curing agent when a water-based paint containing the above hydrophilic resin is constituted. Therefore, said monomer serves to satisfactorily attain the fundamental performance characteristics required of water-based paints.

Said hydrophilic resin contains the hydrophobic resin (B) graft-bonded by transesterification and thus has a structure different from the core/shell structure resulting for mere blending. Therefore, it is stable against phase separation and contributes to the improvement in storage stability as water-based paints and in performance characteristics of coating films.

The acrylic resin (A) to be graft-bonded to polyester resin (B) can be produced by copolymerizing the carboxyl-terminated acrylic monomer (a), the hydroxyl-containing acrylic monomer (b) and the acrylic monomer (c) containing a saturated hydrocarbon group containing 6 to 18 carbon atoms. When necessary, another ethylenically unsaturated monomer (d) may be added as a comonomer in the above copolymerization.

As said carboxyl-terminated acrylic monomer (a), there may be mentioned, among others, half esters resulting from the reaction of a hydroxyalkyl (meth)acrylate and a carboxylic acid anhydride.

The term "(meth)acrylate" as used herein means a methacrylate and/or acrylate.

As said hydroxyalkyl (meth)acrylate, there may be mentioned, for example, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and 4-hydroxybutyl (meth)acrylate.

Said carboxylic acid anhydride includes succinic anhydride, glutaric anhydride, maleic anhydride, phthalic anhydride, hexahydrophthalic anhydride and

trimellitic anhydride, among others.

As other examples of said carboxyl-terminated acrylic monomer (a), there may be mentioned reaction products from a hydroxyalkyl (meth)acrylate- ϵ -caprolactone adduct and a carboxylic acid anhydride and, further, reaction products from a hydroxyalkyl (meth)acrylate-neopentyl glycol carbonate adduct and a carboxylic acid anhydride, among others.

A commercial grade of 2-hydroxyethyl acrylate- ϵ -caprolactone is available from Daicel Chemical Industries, Ltd. under the trademark Placel FA-1, and a commercial grade of a 2-hydroxyethyl methacrylate- ϵ -caprolactone adduct is also available from the same supplier under the trademark Placel FM-1. Reaction products from a hydroxyalkyl (meth)acrylate-neopentyl glycol carbonate adducts and carboxylic acid anhydrides are disclosed in Japanese Kokai Tokkyo Koho H08-157424. Said neopentyl glycol carbonate is also called 5,5-dimethyl-2-oxo-1,3-dioxane or dimethyl-trimethylene carbonate.

Hexahydrophthalic anhydride is preferred as said carboxylic acid anhydride. As regards said carboxyl-terminated acrylic monomer (a), it is preferred that the carboxyl group is remote from the polymerization site. Therefore, reaction products from hydroxyalkyl (meth)acrylate-neopentyl glycol carbonate adducts and carboxylic acid anhydrides are preferred.

The carboxyl-containing monomer (a) may occur as a single compound or a mixture. For the copolymers to have a sufficiently high structural viscosity, it is preferred, however, that a monomer comprising an ring-opened form of neopentyl glycol carbonate as disclosed in Japanese Kokai Tokkyo Koho H08-157424 account for at least 30 mole percent of the whole of monomer (a).

Specific examples of monomer (b) are, typically

those hydroxyalkyl (meth)acrylates such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, 4-hydroxybutyl acrylate, Placel FA-1, Placel FM-1 and hydroxyalkyl (meth)acrylate-neopentyl glycol carbonate adduct.

Specific examples of monomer (c) are alkyl (meth)acrylates containing 6 to 8 carbon atoms such as hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate and stearyl (meth)acrylate, and cyclohexyl (meth)acrylate. Mention may also be made of adducts of glycidyl (meth)acrylate and an alkanolic acids containing 6 to 18 carbon atoms, such as caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid and stearic acid. Mention may further be made of adducts of (meth)acryl isocyanate and alkanols containing 6 to 18 carbon atoms, such as 2-ethylhexanol, lauryl alcohol and stearyl alcohol.

Specific examples of said another ethylenically unsaturated monomer (d) are (meth)acrylate esters such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, t-butyl (meth)acrylate and isobutyl (meth)acrylate, styrene and derivatives thereof, such as styrene, α -methylstyrene and vinyltoluene, nitrile and amide monomers such as acrylonitrile, acrylamide, N,N-dimethyl(meth)acrylamide and N,N-dibutyl(meth)acrylamide, and olefins such as ethylene and propylene.

Since the copolymer should have an acid value of 10 to 100, preferably 20 to 60, and a hydroxyl value of 50 to 300, preferably 60 to 250, the monomer composition has to meet these requirements. Specifically, a monomer composition with which a desired acid value and hydroxyl value can be obtained may be selected by using 2 to 60% by weight, preferably 4 to 40% by weight, of monomer (a), 2 to 40% by weight of monomer (b), 30 to 80% by weight,

preferably 40 to 60% by weight, of monomer (c), and monomer (d) accounting for the balance.

It is recommended that the copolymer have a number average molecular weight of 5,000 to 100,000, preferably 10,000 to 80,000. The polymerization may be carried out by the solution polymerization technique. The acrylic resin (A) is bound to the polyester resin (B) in the manner of grafting. For that purpose, the polymerization for producing (A) may be carried out in a solution of polyester resin (B) synthesized in advance, or both resins may be separately synthesized and bound together by transesterification. In the latter case, both resins in the form of solutions are mixed together and heated at 130 to 200°C.

As is well known, the polyester resin is produced by subjecting a polybasic carboxylic acid and a polyhydric alcohol, as essential components, to polycondensation. It may contain, as other components, a small proportion of a monocarboxylic acid, a hydroxycarboxylic acid, a lactone and/or the like.

Examples of the polybasic carboxylic acid are aromatic polybasic carboxylic acids and anhydrides, such as phthalic anhydride, isophthalic acid, terephthalic acid, trimellitic anhydride, tetrabromophthalic anhydride, tetrachlorophthalic anhydride and pyromellitic anhydride; alicyclic polybasic carboxylic acids and anhydrides, such as hexahydrophthalic anhydride, tetrahydrophthalic anhydride and 1,4- and 1,3-cyclohexanedicarboxylic acid; and aliphatic polybasic carboxylic acids and anhydrides, such as maleic anhydride, fumaric acid, succinic anhydride, adipic acid, sebacic acid and azelaic acid. These may contain one or more of hydroxybenzoic acid, hydroxypivalic acid, 12-hydroxystearic acid and the like; and monocarboxylic acids, such as benzoic acid and t-butylbenzoic acid, in

small proportions.

The polyhydric alcohol includes diols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-diethyl-1,3-propanediol, neopentyl glycol, 1,9-nonanediol, 1,4-cyclohexanedimethanol, neopentyl glycol hydroxypivalate, 2-butyl-2-ethyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 2,2,4-trimethylpentanediol and hydrogenated bisphenol A; and polyols which are at least trihydric, such as trimethylolpropane, trimethylolethane, glycerin and pentaerythritol.

It is also possible to react a polyester resin with a monoepoxide compound such as Cardura E10 (glycidyl versatate, product of Shell Chemical Company), YOA10, YOA20 or YOA30 (α -olefin monoepoxide, product of Daicel Chemical Industries, Ltd.).

Preferably, the polyester resin (B) has an acid value of less than 15 and a number average molecular weight of 1,000 to 10,000.

The polyester resin with the acrylic resin grafted thereupon should comprise 50 to 90% by weight, preferably 60 to 80% by weight, of acrylic resin (A) and 50 to 10% by weight, preferably 40 to 20% by weight, of polyester resin (B). Upon neutralization with a base for dispersing in an aqueous medium, these proportions allow the formation of a dispersion with a core/shell structure, which shows a high structural viscosity.

The polyester resin after grafting has a number average molecular weight of 9,000 to 200,000, preferably 40,000 to 150,000 and an acid value of 20 to 90, preferably 30 to 70. Said range of number average molecular weight is the range within which dispersion in water is possible and strong and durable coating films can be formed. Said acid value range, too, is the range within which dispersion in water is possible and a desired high

structural viscosity can be attained.

Water-based paint

The thus-produced acryl-modified polyester resin is neutralized with a base and dispersed in water. The neutralizing base is used in an amount of 0.3 to 1.4 equivalents, preferably 0.5 to 1.2 equivalents, relative to the acid value of the resin. Usable as the base are inorganic bases such as alkali metal hydroxides and aqueous ammonia; and amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, isopropylamine, diisopropylamine, diethylenetriamine, triethylenetetramine, monoethanolamine, diethanolamine, 2-methyl-2-aminopropanol, morpholine, N-methylmorpholine, N-ethylmorpholine, piperazine, dimethylethanolamine, diethylethanolamine and dimethyldodecylamine. Among these, triethylamine, dimethylethanolamine and diethylethanolamine are preferred.

Paint preparation can be carried out by dispersing a curing agent, a pigment and one or more conventional additives in the aqueous varnish comprising the thus-neutralized acryl-modified polyester dispersed in aqueous medium.

Curing agents for polyester resins are well known in the field of paints. One class includes amino resins, more specifically di-, tri-, tetra-, penta- and hexamethylolmelamine and alkyl etherification products derived therefrom (the alkyl being methyl, ethyl, propyl, isopropyl, butyl, isobutyl and the like), urea-formaldehyde condensates, urea-melamine cocondensates and the like. Preferred are melamine resins.

When an amino resin is used as the curing agent, a sulfonic acid, such as paratoluenesulfonic acid, dodecylbenzenesulfonic acid or dinonylnaphthalene-sulfonic acid; and a salt of such a sulfonic acid with

structural viscosity can be attained.

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When an amino resin is used as the curing agent, a sulfonic acid, such as paratoluenesulfonic acid, dodecylbenzenesulfonic acid or dinonylnaphthalene-sulfonic acid; and a salt of such a sulfonic acid with

an amine which dissociates at the baking temperature for coating films can be used as a catalyst.

A blocked polyisocyanate compound derived from the corresponding polyisocyanate by blocking with a blocking agent may also be used as a curing agent.

Examples of the polyisocyanate compounds are aliphatic diisocyanates such as hexamethylene diisocyanate (HMDI) and trimethylhexamethylene diisocyanate; alicyclic diisocyanates such as isophoronediiisocyanate (IPDI); araliphatic diisocyanates such as xylylene diisocyanate (XDI); aromatic diisocyanates such as tolylene diisocyanate (TDI) and 4,4'-diphenylmethanediisocyanate (MDI); dimers and trimers of these diisocyanates; and adducts of said diisocyanates with a polyhydric alcohol such as trimethylolpropane or with water.

The blocking agent includes oximes such as methyl ethyl ketoxime, acetoxime, cyclohexanone oxime, acetophenone oxime and benzophenone oxime; phenols such as m-cresol and xylenol; alcohols such as methanol, ethanol, butanol, 2-ethylhexanol, cyclohexanol and ethylene glycol monoethyl ether; lactams such as ϵ -caprolactam; diketones such as malonic acid diesters and acetoacetic acid esters; and mercaptans such as thiophenol. Polyisocyanate compounds blocked with diketones (active methylene-containing compounds) are preferred. When blocked polyisocyanate compounds are used, a tin compound such as dibutyltin dilaurate may be added as a catalyst.

The water-based paint of the present invention may contain one or more conventional pigments. Examples thereof are color pigments and glitters or luster pigments, such as titanium dioxide, zinc oxide, carbon black, yellow iron oxide, various lake pigments, aluminum flake and titanium mica; and extenders pigment, such as calcium

carbonate, barium sulfate and clay. The pigments, together with a resin for dispersion, are worked up into pigment pastes, which are then added, together with another or other ingredients, to water varnishes. Other
5 conventional additives such as antipopping, dispersants and surface modifiers may of course be added.

The water-based paint of the present invention is particularly suited for use in providing base coats which are used in finishing coating of automotive bodies, for
10 instance. In this coating process, the metallic or solid color base paint according to the present invention is applied to the surface provided with an electrodeposition coating and an intermediate coat, and a solution-type, water-based or powder clear coat paint is further applied
15 thereonto in the wet-on-wet manner, whereafter both can be baked simultaneously for finishing.

EXAMPLES

In the following production examples and examples,
20 "part(s)" and "%" are on the weight basis, unless otherwise specified.

Polyester resin (B)

Production Example 1

25 A reaction vessel was charged with 613 parts of 1,9-nonanediol, 114 parts of trimethylolpropane, 105 parts of adipic acid and 536 parts of phthalic anhydride, together with 30 parts of xylene. The temperature was raised and the water formed by the reaction was removed
30 by azeotropic distillation with xylene.

From the beginning of reflux, stirring and dehydration were continued while the temperature was raised to 190°C over about 2 hours, until the acid value corresponding to the carboxylic acids amounted to 85.
35 The reaction mixture was then cooled to 140°C. While

maintaining this temperature, 205 parts of Cardura E10 (glycidyl versatate, product of Shell Chemical Company) was added dropwise over 30 minutes, followed by 2 hours of stirring for completing the reaction. A polyester resin with an acid value of 5, a hydroxyl value of 120 and a number average molecular weight of 2,350 was obtained.

Carboxyl-terminated acrylic monomer (a)

10 Production Example 2

A reaction vessel was charged with 130 parts of 2-hydroxyethyl methacrylate, 154 parts of hexahydrophthalic anhydride and 0.142 g of 4-methoxyphenol, and the contents were heated to 120°C while blowing air thereinto. The same temperature was maintained for 30 minutes with stirring and air bubbling and, after confirmation by IR spectrometry of disappearance of the acid anhydride absorption at about 1,800 cm⁻¹, the reaction mixture was cooled. By adding the liquid obtained dropping to methanol, it was confirmed that no gel component was contained. Furthermore, molecular weight calculation was performed based on the measured acid value, whereupon it was confirmed that the calculated value and theoretical value were in agreement.

25

Production Example 3

A carboxyl-terminated acrylate ester monomer was synthesized from 4-hydroxybutyl acrylate and phthalic anhydride in the same manner as in Production Example 2.

30

Production Example 4

A carboxyl-terminated methacrylate ester monomer was synthesized from Placel FM-1 (2-hydroxyethyl methacrylate/ε-caprolactone (1/1) adduct, product of Daicel Chemical Industries, Ltd.) and succinic anhydride

35

in the same manner as in Production Example 2.

Production Example 5

5 A carboxyl-terminated methacrylate ester monomer was synthesized from a 2-hydroxyethyl methacrylate/neopentyl glycol carbonate (1/1) adduct and hexahydrophthalic anhydride in the same manner as in Production Example 2.

10 Acrylic resin (A)

Production Example 6

A reaction vessel was charged with 40.0 parts of S-150 (aromatic hydrocarbon solvent, product of Shoei Kagaku Kogyo) and 21.3 parts of methyl isobutyl ketone (MIBK), the temperature was raised to 100°C with stirring in a nitrogen atmosphere, and a mixture of 7.3 parts of 2-ethylhexyl methacrylate, 48.8 parts of the monomer prepared in Production Example 5 and 1.5 parts of Kayaester O (initiator, product of Kayaku Akzo) was added dropwise at a constant rate over 3 hours. After completion of the dropping, stirring was continued for 30 minutes and then a solution composed of 0.15 part of Kayaester O and 20 parts of S-150 was added dropwise at a constant rate over 30 minutes. After completion of the dropping, stirring was continued for 1 hour to drive the reaction to completion. An acrylic resin with an acid value of 46.8, a hydroxyl value of 117.4 and a number molecular weight of 67,000 was obtained.

30 Production Examples 7 to 12

Modifying the formulation, acrylic resins shown in Table 1 were obtained in the same manner as in Production Example 6.

Table 1

	Production Example											
	6	7	8	9	10	11	12					
S-150	40.0	30.0	30.0	30.0	30.0	30.0	30.0					
MIBK	21.3	13.0	13.0	13.0	13.0	13.0	13.0					
HEA ¹⁾	21.3	30.0	25.0	12.0	20.8	-	-					
4-HBA ²⁾	-	-	-	18.2	-	40.0	40.0					
MAA ³⁾	-	-	2.0	6.1	-	-	-					
EHMA ⁴⁾	71.3	22.0	-	-	62.5	50.0	56.3					
ST ⁵⁾	-	4.0	48.0	53.0	9.1	21.3	15.0					
Monomer of Prodn.Ex.2	-	-	-	-	29.8	-	-					
Monomer of Prodn.Ex.3	-	-	-	-	-	28.3	-					
Monomer of Prodn.Ex.4	-	-	-	-	-	-	63.5					
Monomer of Prodn.Ex.5	48.8	44.0	25.0	10.7	-	-	-					
Kayaester O	3.0	1.0	1.0	1.1	1.0	0.7	4.0					
Acid Value	46.8	59.6	46.9	54.3	48.2	47.0	59.2					
Hydroxyl Value	117.4	233.7	194.8	164.4	132.6	111.6	89.2					
Number average												
Molecular weight	22,000	62,000	49,000	55,000	58,000	74,000	10,000					

1) HEA : 2-ethylhexyle acrylate

2) 4-HBA: 4-hydroxybutyl acrylate

3) MAA : methacrylic acid

4) EHMA: 2-ethylhexyl methacrylate

5) ST : styrene

Hydrophilic resin

Production Example 13

A reaction vessel was charged with 20 parts of S-150, 17 parts of MIBK and 20 parts of the polyester resin prepared in Production Example 1, the temperature was raised to 100°C with stirring in a nitrogen atmosphere and a mixture of 17 parts of 2-hydroxyethyl acrylate, 57 parts of 2-ethylhexyl methacrylate, 39 parts of the acrylic monomer prepared in Production Example 5 and 1.2 parts of Kayaester O was added dropwise at a constant rate over 3 hours. After completion of the dropping, stirring was continued for 30 minutes and then a solution composed of 0.12 part of Kayaester O and 20 parts of S-150 was added dropwise at a constant rate over 30 minutes. After completion of the dropping, stirring was continued at the same temperature for 1 hour. Thereafter, the reaction temperature was raised to 140°C and, while maintaining the temperature, stirring was continued in a nitrogen atmosphere for 4 hours. An acryl-grafted polyester resin with an acid value of 40, a hydroxyl value of 80 and a number average molecular weight of 99,000 was obtained.

The reaction mixture was cooled to 60°C, the nitrogen stream was discontinued, and the mixture was neutralized to a neutralization degree of 100% with dimethylethanolamine (DMEA) and stirred for 30 minutes. Thereto was added deionized water at a constant rate over 1 hour so that the nonvolatile matter content amounted to 25%. Stirring was further continued for 1 hour while maintaining the temperature at 60°C to give a water-based varnish. The varnish had a thixotropy index (TI value) of not less than 4, showing a high structural viscosity.

Production Examples 14-18 and Comparative Examples 1 and 2

35 Modifying the formulation, water varnishes shown in

Table 2 were obtained in the same manner as in Production Example 13.

Table 2

	Comparative Example		Production Example									
	1	2	13	14	15	16	17	18				
Polyester resin	20	20	20	50	20	33	20	20				
S-150	28	28	40	28	28	28	28	28				
MIBK	12	12	17	12	12	12	12	12				
HEA	17	17	17	15	20	8	-	-				
4-HBA	-	-	-	-	-	12	17	17				
MAA	6	6	-	-	1.6	5	-	-				
EHMA	57	30	57	11	-	-	40	45				
St	-	27	-	2	38.4	35	17	12				
Monomer of Prodn.Ex.2	-	-	-	-	-	-	22.6	-				
Monomer of Prodn.Ex.3	-	-	-	-	-	-	-	-				
Monomer of Prodn.Ex.4	-	-	39	22	20	7	-	50.8				
Kayaester P	0.8	0.8	1.2	0.5	0.8	0.7	0.8	0.8				
Acid Value	40	40	40	30	40	40	45	55				
Hydroxyl Value	100	100	80	75	95	90	63	70				
Number average Molecular weight	120,000	101,000	50,000	100,000	102,100	67,000	100,000	45,000				
‡ Neutralization with DMEA	140	140	100	120	100	80	120	90				
Viscosity of water Varnish (TI value)	2	1.8	>4	>4	>4	3.7	2.7	2.8				

Viscosity of water varnish : expressed in terms of the thixotropy index (TI) value
 TI value = (viscosity at 6 rpm)/(viscosity at 60 rpm)[20°C type B viscometer]

Resin for dispersion

Production Example 19

A reaction vessel was charged with 400 parts of diethylene glycol monobutyl ether (BDG) and, under stirring at 100°C, a monomer mixture composed of 100 parts of styrene, 172 parts of methyl methacrylate, 230 parts of lauryl acrylate, 219 parts of methyl acrylate, 218 parts of Placel FM-1 (product of Daicel Chemical Industries, Ltd.), 61 parts of methacrylic acid and 10 parts of Kayaester O was added dropwise at a constant rate over 3 hours and, 30 minutes later, 50 parts of BDG and 3 parts of Kayaester O were further added dropwise over 30 minutes. At that temperature, the reaction was further conducted for 1 hour to give an acrylic resin with an acid value of 40, a hydroxyl value of 50 and a number average molecular weight of 17,000 (this is referred to as "resin for dispersion").

The thus-obtained resin for dispersion was heated to 85°C with stirring and solubilized in water by adding 87 parts of triethylamine and 2,952 parts of deionized water to give a transparent, viscous, aqueous solution. The solid content of the aqueous solution obtained was 22%.

25 Pigment dispersion paste

Production Example 20

A pigment dispersion paste was obtained by adding 42 parts of titanium dioxide and 10 parts of barium sulfate to 100 parts (on the nonvolatile matter basis) of the resin for dispersion as prepared in Production Example 19 and stirring the mixture with Disper.

Powder clear paint

Production Example 21

35 1. Acrylic resin varnish

A reaction vessel was charged with 630 parts of xylene and the temperature was raised to 130°C. Using a dropping funnel, a mixture of 200 parts of styrene, 450 parts of glycidyl methacrylate, 270 parts of methyl methacrylate, 80 parts of isobutyl methacrylate and 75 parts of Kayaester O was added dropwise at a constant rate over 3 hours. After completion of the dropping, the same temperature was maintained for 30 minutes. Then, a solution composed of 1 part of Kayaester O and 70 parts of xylene was further added dropwise over 30 minutes. After completion of the dropping, the reaction was further continued at 130°C for 1 hour. The xylene was then removed by distillation under reduced pressure to give an acrylic resin varnish.

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2. Powder clear paint

In a Henschel mixer (product of Mitsui Miike Machinery Co.), 70 parts of the acrylic resin varnish obtained in the above manner, 19.1 parts of decanedicarboxylic acid, 0.11 part of CF-1056 (product of Toray Dow Corning Silicone) and 0.89 part of benzoin were dry-mixed. Then, the mixture was melted at 100°C for effecting dispersion in a Cokneader PR-46 (product of Buss, Switzerland). After cooling the mixture was ground in a hammer mill and classified using a 150-mesh wire gauze to give a powder acrylic clear paint.

Example 1 to 6 and Comparative Examples 3 and 4
Water-based metallic base paints [1] to [8] were prepared according to the formulations shown in Table 3.

An aluminum pigment (Aluminum Paste NW-91-2061, aluminum metal pigment 62%, product of Toyo Aluminium) was uniformly blended in advance with the resin for dispersion, or with the pigment dispersion paste when it was added. The acryl-grafted polyester resin component

and curing agent were mixed together in advance. When the melamine resin was used as the curing agent, it was mixed with the acryl-grafted polyester resin and dissolved in water on the occasion of dissolving said resin in water. Thereafter, the resin-curing agent mixture was uniformly blended with the pigment and other components. Then, the additive was further added, and the water-based metallic base paints were prepared using a stirrer at room temperature. The aluminum pigment was added in an amount of 11.4 to 12.5 parts per 100 parts of the resin solids. In Table 3, C-212 indicates a Mitsui Cytec's methyl/butyl melamine resin curing agent, and BL-116 indicates a Sumitomo Bayer's blocked isocyanate curing agent. BYK-341 indicates a BYK Chemie Japan's silicone antipopping agent.

Table 3

	Comparative Example		Production Example							
	3	4	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]
Water based metallic Base paint										
Hydrophilic Resin	Comparative Example 1	66.5	-	-	-	-	-	-	-	-
	Comparative Example 2	-	66.5	-	-	-	-	-	-	-
	Production Example 13	-	-	66.5	-	-	-	-	-	-
	Production Example 14	-	-	-	66.5	-	-	-	-	-
	Production Example 15	-	-	-	-	49.5	-	-	-	-
	Production Example 16	-	-	-	-	-	-	66.5	-	-
	Production Example 17	-	-	-	-	-	-	-	66.5	-
	Production Example 18	-	-	-	-	-	-	-	-	66.5
Curing agent	C-212	28.5	-	-	-	28.5	28.5	28.5	28.5	28.5
	BL-116	-	28.5	28.5	-	-	-	-	-	-
Pigment dispersion Paste Aluminum pigment		-	-	-	-	-	4.1	-	-	-
		10	10	10	10	10	10	10	10	10
Resin for dispersion		5	5	5	5	5	17	5	5	5
Additive		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	BYK-341									
Viscosity of water varnish(TI value)		1.3	1.1	1.1	3.4	3.3	2.9	2.4	2.5	2.4

In the table, the amount of the resins are on the solids basis
 Viscosity of water varnish : expressed in term of the thixotropy index (TI) value
 $TI \text{ value} = (\text{viscosity at } 6 \text{ rpm}) / (\text{viscosity at } 60 \text{ rpm}) [20^\circ\text{C, type B viscometer}]$

Evaluation Tests

To the water-based metallic base paints [2] and [3] was added 1 part of Nacure 5225 (amine-blocked acid catalyst, product of King Industries Inc.). The viscosity was then adjusted to 60 seconds (Ford cup No. 4) by dilution with deionized water. The water-based metallic base paints [1] and [4] to [8] were subjected to viscosity adjustment in the same manner without adding the acid catalyst. The thus-viscosity-adjusted water-based metallic base paints [1] to [8] were applied, by spraying to a dry film thickness of 10 to 50 μm , to steel sheets provided beforehand with an intermediate coat, followed by drying at 80°C for 10 minutes.

Then, a clear paint was applied to a dry film thickness of 40 μm . After 5 minutes of setting, the base coat and clear coat were simultaneously baked at 140°C for 30 minutes.

The paints of Examples 1 to 6 and Comparative Examples 3 and 4 were evaluated for workability by the method mentioned below. As regards the painting conditions, the temperature was 25°C and two levels of humidity, namely 65% and 85%, were employed.

The water-based metallic base paints used were respectively evaluated also for storage stability by the method mentioned below. The results are collectively shown in Table 4.

Evaluation methods

1. Threshold film thickness for sagging

The maximum film thickness at which no sagging-due film deficiency was observed on a coating film provided by gradient coating from 10 μm (thinnest portion) to 50 μm (thickest portion) was defined as the threshold film thickness for sagging. When the threshold film thickness for sagging was not less than 25 μm , the paint was regarded

as satisfactory. The paints of Examples 1 to 6 were all satisfactory.

2. Threshold film thickness for popping

5 The maximum film thickness at which no popping-due
film deficiency was observed on a coating film provided
by gradient coating from 10 μm (thinnest portion) to 50
 μm (thickest portion) was defined as the threshold film
thickness for popping. When the threshold film thickness
10 for popping was not less than 25 μm , the paint was regarded
as satisfactory. The paints of Examples 1 to 6 were all
satisfactory.

3. Storage stability

15 The initial stability immediately after dilution
and the state of dispersion of the diluted paint after
10 days of standing at 40°C were evaluated by the eye.

Table 4

	Comparative Example		Production Example					
	3	4	1	2	3	4	5	6
Clear paint	PD	O-150	O-150	O-150	O-150	PD	PD	O-150
Water-based metallic base paint	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]
Humidity 65%	Sagging limit (μm) Popping limit (μm)	30 26	50 30	52 33	55 37	47 36	40 28	43 29
Humidity 85%	Sagging limit (μm) Popping limit (μm)	10 20	45 26	47 30	48 30	44 29	36 25	35 24
Storage Stability Initial	H	H	H	H	H	H	H	H
After Standing	H	PS	H	H	H	H	H	H

Clear paint : PD---Powder clear paint

O-150---Nippon Paint's melamine clear paint superlac o-150

Sagging limit : threshold film thickness for Sagging

Popping limit : threshold film thickness for Popping

H : homogeneous

PS : partially sedimented

CLAIMS

1. A hydrophilic resin which comprises 50 to 90% by weight of an acrylic resin (A) and 50 to 10% by weight of a polyester resin (B), said acrylic resin (A) being graft-bonded to said polyester resin (B) by means of transesterification, wherein said acrylic resin (A) comprises a carboxyl-terminated acrylic monomer (a), a hydroxyl-containing acrylic monomer (b) and an acrylic monomer (c) containing a saturated hydrocarbon group containing 6 to 18 carbon atoms, and has an acid value of 10 to 100, a hydroxyl value of 50 to 300 and a number average molecular weight of 5,000 to 100,000.

2. The hydrophilic resin according to Claim 1, wherein said carboxyl-terminated acrylic monomer (a) comprises a reaction product of one compound (a-1) selected from the group consisting of hydroxyalkyl (meth)acrylates, hydroxyalkyl (meth)acrylate-ε-caprolactone adducts and hydroxyalkyl (meth)acrylate-neopentyl glycol carbonate adducts, with one carboxylic acid anhydride (a-2) selected from the group consisting of succinic anhydride, glutaric anhydride, maleic anhydride, phthalic anhydride, hexahydrophthalic anhydride and trimellitic anhydride.

3. The hydrophilic resin according to Claim 2, wherein at least 30 mole percent of said carboxyl-terminated acrylic monomer (a) comprises a reaction product of said hydroxyalkyl (meth)acrylate-neopentyl glycol carbonate adduct, with said carboxylic acid anhydride (a-2).

4. The hydrophilic resin according to Claim 1, 2 or 3, wherein said hydroxyl-containing acrylic monomer

(b) comprises at least one compound selected from the group consisting of 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and 4-hydroxybutyl (meth)acrylate.

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5. The hydrophilic resin according to Claim 1, 2, 3 or 4, wherein said acrylic monomer(c) containing a saturated hydrocarbon group containing 6 to 18 carbon atoms is one compound selected from the group consisting of alkyl (meth)acrylates containing 6 to 18 carbon atoms, cyclohexyl (meth)acrylate, reaction products of glycidyl (meth)acrylate with an alkanolic acid containing 6 to 18 carbon atoms, and reaction products of (meth)acryl isocyanate with an alkanol containing 6 to 18 carbon atoms.

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6. The hydrophilic resin according to Claim 1, 2, 3, 4 or 5, wherein said polyester resin (B) has an acid value of less than 15 and a number average molecular weight of 1,000 to 10,000.

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7. A water-based paint which comprises the hydrophilic resin according to Claim 1, 2, 3, 4, 5 or 6, a curing agent and pigment, dispersed in an aqueous medium containing a neutralizing base.

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8. A method of coating by two coat one bake technique which comprises applying the water-based paint according to Claim 7 to a substrate and then applying a clear paint, followed by baking.

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9. A coated article having a coat resulting from application of the water-based paint according to Claim 7.

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10. A hydrophilic resin substantially as hereinbefore described with reference to the Examples.



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Claims searched: 1-10

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Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.P): C3P - PFC
Int CI (Ed.6): C08F 283/00, 283/01, 283/02; C08G 81/02
Other: Online - WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 1356624 (Kansai Paint) - claims and Example 7	1-10
X,P	EP 0781797 A2 (Nippon Paint) - claims and Example 1	1-10
X	EP 0185431 A2 (Nippon Paint) - claims and Example 4	1-10

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